

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

REC'D 28 JUN 1999

WIPO PCT

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| Applicant's or agent's file reference 1505-49879 | FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416) | |
| International application No. PCT/US98/05782 | International filing date (day/month/year) 24 MARCH 1998 | Priority date (day/month/year) 25 MARCH 1997 |
| International Patent Classification (IPC) or national classification and IPC Please See Supplemental Sheet. | | |
| Applicant THE STATE OF OREGON ACTING BY AND THROUGH THE STATE BOARD OF HIGHER EDUCATION | | |

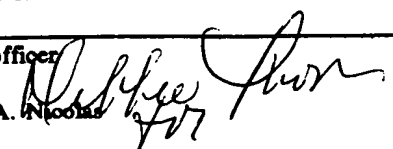
- This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
- This REPORT consists of a total of 8 sheets.

☐ This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority. (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 0 sheets.

- This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of report with regard to novelty, inventive step or industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☒ Certain documents cited
- VII ☒ Certain defects in the international application
- VIII ☒ Certain observations on the international application

| | |
|--|--|
| Date of submission of the demand 15 OCTOBER 1998 | Date of completion of this report 02 JUNE 1999 |
| Name and mailing address of the IPEA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 | Authorized officer  Wesley A. Nicholas |
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International application No.

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I. Basis of the report

1. This report has been drawn on the basis of (Substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments):

☒ the international application as originally filed.

☒ the description, pages 1-22, as originally filed.

pages NONE, filed with the demand.

pages NONE, filed with the letter of _____.

pages _____, filed with the letter of _____.

☒ the claims, Nos. 1-35, as originally filed.

Nos. NONE, as amended under Article 19.

Nos. NONE, filed with the demand.

Nos. NONE, filed with the letter of _____.

Nos. _____, filed with the letter of _____.

☒ the drawings, sheets/fig 1-12, as originally filed.

sheets/fig NONE, filed with the demand.

sheets/fig NONE, filed with the letter of _____.

sheets/fig _____, filed with the letter of _____.

2. The amendments have resulted in the cancellation of:

☒ the description, pages none.

☒ the claims, Nos. none.

☒ the drawings, sheets/fig none.

3. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box Additional observations below (Rule 70.2(c)).

4. Additional observations, if necessary:

NONE

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V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**1. STATEMENT**

| | | | |
|-------------------------------|--------|---------------------------------|-----|
| Novelty (N) | Claims | (Please See supplemental sheet) | YES |
| | Claims | (Please See supplemental sheet) | NO |
| Inventive Step (IS) | Claims | (Please See supplemental sheet) | YES |
| | Claims | (Please See supplemental sheet) | NO |
| Industrial Applicability (IA) | Claims | (Please See supplemental sheet) | YES |
| | Claims | (Please See supplemental sheet) | NO |

2. CITATIONS AND EXPLANATIONS

Claims 1,2,4,6,9, and 11-12 lack novelty under PCT Article 33(2) as being anticipated by Braun et al. (Journal of Less Common Metals, 76 (1980) 33-40).

Braun et al. teach the formation of the new compounds $\text{ThFe}_4\text{P}_{12}$, $\text{ThRu}_4\text{P}_{12}$, and $\text{ThOs}_4\text{P}_{12}$ (page 33, line 1). Furthermore, Braun et al. indicate that the $\text{ThFe}_4\text{P}_{12}$ compound was crystalline (page 34, line 39) and had a cubo-octahedral crystal structure (page 35, line 13). In addition, there are a total of 42 compounds with the $\text{LaFe}_4\text{P}_{12}$ structure that are known (page 37, lines 33-38). In these compounds, the Lanthanum position is occupied by the early (large) lanthanoids or thorium, and the iron and phosphorus places are filled by ruthenium or osmium and arsenic or antimony respectively (page 37, lines 33-38). Braun et al. further disclose that T_4P_{12} (TP3) framework corresponds to that of a binary skutterudite (CoAs_3) compounds TPn_3 , wherein T Co, Rh, or Ir and Pn P, As, or Sb (page 38, lines 6-10).

Claims 1, 6, 9, and 11-12 lack novelty because Braun et al. discloses compounds (page 33, line 1) that are the same as Applicants claim 1 when $x=0$, $y=0$, $M=\text{Th}$, $M'=\text{Fe}$, Ru , or Os , and $M''=\text{P}$.

Claims 2 and 4 lack novelty because Braun et al. disclose that the Th (thorium) can be substituted with early (large) lanthanoids (page 37, lines 33-38).

Claims 1,5,13-14,18-20,26-28, and 30 lack novelty under PCT Article 33(2) as being anticipated by Fleurial et al. (5,610,366).

Fleurial et al. teach of the production of high performance thermoelectric materials. More specifically, p and n-type semiconductors can be formed with the formula $\text{Co}_{1-x}\text{Rh}_x\text{Ir}_y\text{Sb}_3$, wherein $0 \leq x \leq 1$ and $0 \leq y \leq 1$ (col. 2, lines 41-53). Fleurial et al. further disclose that thermoelectric elements fabricated with the said formula having skutterudite-type crystal lattice structures have demonstrated a ZT (thermodynamic figure of merit) of 2 (col. 3, lines 30-31).

Claims 1, 5, 13-14, 18, 19 and 20 lack novelty because when $x \geq 0$ and $y = 0$ in the formula as stated by Fleurial et al., $\text{Co}_{1-x}\text{Rh}_x\text{Sb}_3$ is obtained (col. 2, lines 41-53). In the (Continued on Supplemental Sheet.)

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VI. Certain documents cited

1. Certain published documents (Rule 70.10)

| <u>Application No. Patent No.</u> | <u>Publication Date (day/month/year)</u> | <u>Filing Date (day/month/year)</u> | <u>Priority date (valid claim) (day/month/year)</u> |
|---------------------------------------|--|---|---|
| US, A, 5,726,381 | 10 MARCH 1998 | 10 OCTOBER 1995 | 11 OCTOBER 1994 |

2. Non-written disclosures (Rule 70.9)

Kind of non-written disclosure

Date of non-written disclosure
(day/month/year)

Date of written disclosure
referring to non-written disclosure
(day/month/year)

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VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:

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VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

Claim 12 is objected to as lacking clarity under PCT Rule 66.2(a)(v) because practice of the claimed invention is not adequately described in writing, as required under PCT Rule 5.1(a)(iii), for the reasons set forth in the immediately preceding paragraph.

For example, claim 12 does not further limit claim 11, perhaps the 11 should be changed to a 10.

Claims 1-35 are objected to under PCT Rule 66.2(a)(v) as lacking clarity under PCT Article 6 because the claims indefinite for the following reason(s): Claims 1, 19, 26, 31, and 35 contain the term "doped or undoped" which is critical to the invention. The specification does not define this term. Perhaps the Applicant intends for this term to apply to the doping of the skutterudite with ANY compound.

Claims 26-30 are objected to under PCT Rule 66.2(a)(v) as lacking clarity under PCT Article 6 because the claims are indefinite for the following reason(s): in claim 26, the applicant defines the term N' but there is no N' in the formula. Since it is unclear how claim 26 should be read, the Examiner takes the position that the formula in claim 26 should be like Formula 3 on page 10, line 36 of the Applicants specification.

Supplemental Box

(To be used when the space in any of the preceding boxes is not sufficient)

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Continuation of: Boxes I - VIII

CLASSIFICATION:

The International Patent Classification (IPC) and/or the National classification are as listed below:
IPC(6): HO1L 29/04, 29/06, 35/16, 35/18 and US Cl.: 136/236.1, 238, 239, 240; 257/15, 22, 467, 468, 469, 470, 613, 616, 930; 252/62.3T, 519.13, 519.14, 519.15, 519.4, 520.5, 521.1, 521.2, 521.5

V. 1. REASONED STATEMENTS:

The report as to Novelty was positive (YES) with respect to claims 3,7,8,10, 15-16, 21-25,29,31-35.
The report as to Novelty was negative (NO) with respect to claims 1-2,4-6,9,11-14,17-20,26-28,30.
The report as to Inventive Step was positive (YES) with respect to claims 3,10,15-16,21-25,31-34.
The report as to Inventive Step was negative (NO) with respect to claims 1-2,4-9,11-14,17-20,26-30,35.
The report as to Industrial Applicability was positive (YES) with respect to claims 1-35 .
The report as to Industrial Applicability was negative (NO) with respect to claims n/a.

V. 2. REASONED STATEMENTS - CITATIONS AND EXPLANATIONS (Continued):

instant invention, when $x = 1$, $y \leq 4$, $M' = \text{Rh}$, and $M'' = \text{Sb}$ in the formula (claims 1 and 19), $\text{Co}_x\text{Rh}_{4-y}\text{Sb}_{12}$ is obtained. The two formulas $\text{Co}_{1-x}\text{Rh}_x\text{Sb}_{12}$ and $\text{Co}_x\text{Rh}_{4-y}\text{Sb}_{12}$ are considered the same because they can have the same stoichiometric ratios between elements. Furthermore, when this compound is in a skutterudite crystal lattice, it exhibits a thermodynamic figure of merit (ZT) of 2 (col. 3, lines 30-31).

Claims 26-28 and 30 are objected to because the same formula as the instant invention can be obtained in Fleurial et al. because Fleurial et al. discloses that the compound can be in a skutterudite crystal lattice, i.e. a superlattice. For example, in the instant invention when x and $x' = 1$, y and $y' = 4$, and $M'' = \text{Sb}$, the compound as disclosed by Fleurial et al. is obtained when the Fleurial et al. compound has values of $x = 0$ and $y = 0$ (col. 2, lines 41-53).

Claims 7,8,17,26, and 29 lack an inventive step under PCT Article 33(3) as being obvious over Braun et al. (Journal of Less Common Metals, 76 (1980) 33-40).

Claims 7 and 8 lack an inventive step because the compounds as disclosed by Braun et al. are considered to be the same and therefore have similar characteristics, e.g. nucleation temperature.

Claim 17 lacks an inventive step because Braun et al. discloses compounds (page 33, line 1) that are the same as Applicants claim 1 when $x=0$, $y=0$, $M=\text{Th}$, $M'=\text{Fe}$, Ru , or Os , and $M''=\text{P}$. Since these compounds are considered to be the same, similar compounds have similar decomposition characteristics.

Claims 26 and 29 lack an inventive step because crystal lattices are formed by melting single crystals together and having them reform together as a lattice. Claims 7 and 8 are objected to because the compounds as disclosed by Braun et al. are considered to be the same and therefore have similar characteristics, i.e. nucleation temperature.

Claims 7 and 8 lack an inventive step under PCT Article 33(3) as being obvious over Fleurial et al. because the compounds as disclosed by Fleurial et al. are considered to be the same and therefore have similar characteristics, e.g. nucleation temperature.

Claim 35 lacks an inventive step under PCT Article 33(3) as being obvious over Braun et al. in view of Donohue (US 3,932,291) and Jayadev et al. (US 4,447,277) because Donohue teaches the use of chalcopyrite-type structures in semiconductor materials (col. 1, line 58) and shows that these materials exhibit thermoelectric properties and are crystalline in form (Example 3, col. 6, lines 63-68). In addition, Jayadev et al. teach the use of multiple crystalline phase materials in thermoelectric devices because the multiple crystalline phases increase the thermoelectric properties, i.e. high electrical conductivity and low thermal conductivity (col. 2, lines 57-68).

Donohue further discloses that chalcopyrite has thermoelectric properties (Example 3, col. 6, lines 63-68) which make it suitable for use in thermoelectric materials and Jayadev et al. disclose that it would have been advantageous to have added different crystalline phase material to a thermoelectric device because it would have increased the thermoelectric properties by providing more grain boundaries (col. 2, lines 57-68). The chalcopyrite as disclosed by Donohue consists of a tetragonal structure (col. 1, line 58) whereas the compound of Braun et al. consists of a cubo-octahedral crystal structure (page 35, line 13) which would have made the combination of the two advantageous for an enhancement of thermoelectric properties because of their differing crystalline structures. This mixture is still considered crystalline because it is still possible for long-range crystalline order to be present.

Claims 3,10,15-16,21-25,31-34 meet the criteria set out in PCT Article 33(2)-(4), because the prior art does not

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Supplemental Box

(To be used when the space in any of the preceding boxes is not sufficient)

Continuation of: Boxes I - VIII

Sheet 11

teach or fairly suggest the limitations of compounds used in the skutterudite structure as described in claims 3,10,15-16,21-25, and 31-34.

Claims 1-35 have industrial applicability because the skutterudite compound can be used in thermoelectric devices.

NEW CITATIONS

US 4,447,277 A (Jayadev et al) 8 MAY 1984, see column 2, lines 8-17 and 57-67, column 5, lines 51-55, column 7, lines 18-25, column 8, lines 37-42, column 10, lines 15-18, column 12, lines 10-30.

US 3,932,291 A (Donohue) 13 JANUARY 1976, see column 1, lines 15-58, column 6, lines 60-67

Braun et al. Thorium-Containing Pnictides with the LaFe₄P₁₂ Structure. Journal of Less Common Metals. 1980, Vol. 76, pages 33.